1a) If we are to ignore the second ionization, and we are told that H₂SeO₄ is strong acid (comparable to H₂SO₄) with a complete, first ionization, then the approximate hydronium ion concentration of a 0.1875 M solution would be **0.1875 M**.

b) We are told that we, in fact, can not ignore the second ionization, and therefore must calculate the [H₃O⁺] concentration. We can set up our I.C.F. table for the following reaction:

\[
\text{HSeO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{SeO}_4^{2-}
\]

\[K_{a2} = 1.2 \times 10^{-2}\]

<table>
<thead>
<tr>
<th>I</th>
<th>0.1875</th>
<th>0.1875</th>
<th>0.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>F</td>
<td>0.1875 - x</td>
<td>0.1875 + x</td>
<td>x</td>
</tr>
</tbody>
</table>

Setting up the equilibrium expression, we get (note we can NOT use the approximation, and must solve a quadratic):

\[K_{a2} = 1.2 \times 10^{-2} = \frac{[H_3O^+][SeO_4^{2-}]}{[HSeO_4^-]} = \frac{(0.1875 + x)(x)}{(0.1875 - x)}\]

which leads to a value for \(x = 0.0107\) M, and a \([H_3O^+] = 0.1982\) M. (That’s 5.7% larger, for those keeping track!)

2a) From the Henry’s Law data, we can get the solubility, and therefore, the concentration of H₂CO₃(aq). S = k₃P, so \(S = (0.033)(3.2 \times 10^{-4}) = 1.056 \times 10^{-5}\) M. The overall equilibrium constant we are given can now be used for the \(K_{a1}\) value, since Henry’s Law took care of the first equilibrium. That \(K_{a1} = 4.5 \times 10^{-7}\), and also equals:

\[K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]} = 4.5 \times 10^{-7} = \frac{(x)(x)}{(1.056 \times 10^{-5} - x)}\]

(This last part arose from our normal I.C.E. table.) We need to solve the quadratic explicitly here, so here is the answer: \(x = [H_3O^+] = 1.97 \times 10^{-6}\), and **pH = 5.71**.

b) Well, we could go through a very long and involved calculation to find this, or we could simply remember the concentration of the characteristic anion of an acid = \(K_{a2}\), so in this case \([CO_3^{2-}] = 4.7 \times 10^{-11}\) M.

c) If the pressure doubles, the [H₂CO₃] will become \(3.168 \times 10^{-5}\) M, so we can run our quadratic again to get \(x = [H_3O^+] = 3.557 \times 10^{-6}\), and **pH = 5.45**.

3) We are given a percent by mass, and a density, and are asked to calculate the pH, the hydroxide ion concentration, and the freezing point of an NH₃ solution. The \(K_b\) for NH₃ is 1.8 x 10⁻⁵.

Here is our equilibrium:
NH₃ + H₂O ⇌ NH₄⁺ + OH⁻.

Assume we have one litre of solution, which corresponds to 990 g of solution. Of this mass, 10%, or 99 g is ammonia, and the balance is water, which means we have 891 g of water. 99 g of ammonia correspond to 5.813 moles, which means our concentrations are 5.813 M, and 6.524 M, and we will need them both.

Using our normal I.C.F. table, we come to the equilibrium expression (we can use the approximation):

\[ K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)^2}{(5.813M)} \]

which leads to \( x = 1.022 \times 10^{-2} \) M; since this concentration represents [OH⁻], we know that [OH⁻] = 1.022 \times 10^{-2} M. Our pH = 1.99, which gives us a \( \text{pH} = 12.01 \).

For the freezing point depression, we need to calculate an apparent molality from the above. We are in one litre of solution (891 g of water) and we have (5.813 + 0.01022) moles in solution, giving a molality of 6.536 m. Substituting this molality into \( \Delta T_f = K_f m \), we get: \( \Delta T_f = (1.858 \, ^\circ\text{C}/\text{m})(6.536 \, \text{m}) = 12.143 \, ^\circ\text{C} \). Therefore, our freezing point is: -12.143°C.

4) Since we are working with formic acid, we need a \( K_a = 1.7 \times 10^{-4} \), so \( \text{pK}_a = 3.77 \). We need pH of 3.25, so: \( \text{pH} = \text{pK}_a + \log(\frac{[CHO_2]}{[HCHO_2]}) \) leads us to: 3.25 = 3.77 + \log(\frac{[CHO_2]}{[HCHO_2]}). This leads to: 0.3020 = \frac{[CHO_2]}{[HCHO_2]}.

Formic acid has \( M_m = 46.0257 \) and a given density of 1.220 g/mL. To make the buffer, we need first to make the sodium salt of the formic acid, which we will do by the addition of pure formic acid to the NaOH solution we are given. We have 350 mL (=0.350 L) of 0.0875 M NaOH or 3.06 x 10⁻² moles OH⁻ ion we need to neutralize, for which we will use 3.06 x 10⁻² moles of formic acid, or 1.4084 g which is 3.8226 mL. Call this volume 1.

We now have 3.06 x 10⁻² moles of NaCHO₂.

The important thing to recognize at this point is that, although the total volume of the solution is unknown, it is quite possible to calculate concentrations of both HCHO₂ and CHO₂. As stated above, we have 3.06 x 10⁻² moles of NaCHO₂ in some unknown volume; we will also have a certain number of moles of HCHO₂ in the same unknown volume! From the ratio above \( 0.3020 = \frac{[CHO_2]}{[HCHO_2]} \), we find we need an additional 1.013 x 10⁻¹ moles HCHO₂ or 4.6635 g which is 3.8226 mL. Call this volume 2. The total volume we need, therefore, is volume₁ + volume₂ = 1.1544 mL + 3.8226 mL = 4.9770 mL.

5) A solution can certainly have \([H_3O^+] = 2 \times [OH^-]\), which would correspond to a pH of 6.85. A solution can also have a pH = 2 x pOH, which would correspond to a pH of 9.33, but these can not be the same solution! For the first part: \( K_w = [H_3O^+][OH^-] = (2x)(x) = \) ...
$10^{-14}$, and $x = 7.07 \times 10^{-8}$ M, so $[H_3O^+] = 1.414 \times 10^{-7}$. For the second part, $14 = \text{pH} + \text{pOH} = 2x + x$, and $x = 4.67$, so pH = 9.33.